PATENT SPECIFICATION

(11) 1291609

1291609

NO DRAWINGS

(21) Application No. 63157/69 (22) Filed 29 Dec. 1969

(31) Convention Application No. 525 (32) Filed 28 Dec. 1968 in

(33) Japan (JA)

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(54) MODIFIED POLYPHENYLENE OXIDES AND METHOD FOR PRODUCTION THEREOF

(71) We, SUMITOMO CHEMICAL COMPANY, LTD., a Corporation organized under the laws of Japan, of 15, Kitahama-5-chome, Higashi-ku, Osaka, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to a method for producing modified polyphenylene oxides which oxides having excellent properties which have not been seen heretofore.

Processes for polymerizing styrenes in the presence of a polyphenylene oxide and a rubber component have already been disclosed in Dutch Patent Application No. 66-17529 and French Patent No. 1,551,503. That is, it is well known to polymerize styrene in a suspension type aqueous dispersion in the presence of a polyphenylene oxide and a rubber component. However, in the process disclosed in

PATENTS ACT 1949

SPECIFICATION NO 1291609

Reference has been directed, in pursuance of Section 9, subsection (1) of the Patents Act 1949, to Specification No 1254337

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inventors previously found a process carried out by graft-polymerizing styrene type compounds on the polyphenylene oxides. It was found that unlike the conventionally known mixtures of polyphenylene oxides with polystyrenes, the thus graft-copolymerized and modified polyphenylene oxides have been improvide in moldability without being greatly injured in properties inherent to the polyphenylene oxides.

As the result of further studies the inventors have been able to find such facts as mentioned below. That is, in carrying out the graft-copolymerization of polyphenylene oxides with styrene type compounds in the presence of a rubbery polymer, the resulting modified polyphenylene oxide resins have excellent properties without being substantially injured in heat resistance inherent thereto, contrary to the fact that when a rubbery polymer is mixed with a different polymer, the resulting mixture is lowered in heat resistance, in general. Thus, the present invention provides a novel method capable of giving modified polyphenylene type compound in a solvent in the presence of a radical-initiator as a catalyst, the conversion is greatly affected by the monomer concentration, and a conversion of more than 80% cannot be attained unless the monomer concentration is more than 70% by weight, and if the monomer concentration is less than 70% by weight, e.g. 20% by weight, the conversion does not reach more than about 25%. Accordingly, the above-mentioned process is commercially disadvantageous. Further, in polymerizing a styrene compound in the presence of a polyphenylene oxide, the polyphenylene oxide inhibits or suppresses the polymerization of the styrene compound since said polyphenylene oxide contains a phenolic hydroxyl group, and the conversion of the styrene type compound is made lower than in the case where the polymerization is effected in the absence of polyphenylene oxide. Particularly when the amount of the polyphenylene oxide is large, there are some cases where the polymerization does not progress at all.

Such phenomena as mentioned above are ob-

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This invention relates to a method for producing modified polyphenylene oxides which have been more improved in properties than those obtained according to conventional processes.

Polyphenylene oxides have been known as resins excellent in such properties as heat resistance, chemical resistance and mechanical and electrical properties, but have draw-backs such that they are relatively low in moldability due to their inherently high softening points.

With an aim to improve polyphenylene oxides in moldability without injuring the excellent properties inherent thereto, the present inventors previously found a process carried out by graft-polymerizing styrene type compounds on the polyphenylene oxides. It was found that unlike the conventionally known mixtures of polyphenylene oxides with polystyrenes, the thus graft-copolymerized and modified polyphenylene oxides have been improvide in moldability without being greatly injured in properties inherent to the polyphenylene oxides.

As the result of further studies the inventors have been able to find such facts as mentioned below. That is, in carrying out the graft-copolymerization of polyphenylene oxides with styrene type compounds in the presence of a rubbery polymer, the resulting modified polyphenylene oxide resins have excellent properties without being substantially injured in heat resistance inherent thereto, contrary to the fact that when a rubbery polymer is mixed with a different polymer, the resulting mixture is lowered in heat resistance, in general. Thus, the present invention provides a novel method capable of giving modified polyphenylene oxides having excellent properties which have not been seen heretofore.

Processes for polymerizing styrenes in the presence of a polyphenylene oxide and a rubber component have already been disclosed in Dutch Patent Application No. 66-17529 and French Patent No. 1,551,503. That is, it is well known to polymerize styrene in a suspension type aqueous dispersion in the presence of a polyphenylene oxide and a rubber component. However, in the process disclosed in said Dutch Patent Application, styrene is used in an amount far larger than the polyphenylene oxide. Further, in the process of said French Patent also, styrene is used in more than about 3 times the amount of the polyphenylene oxide. It should therefore be said that these processes are techniques for the modification of polystyrenes rather than those for the modification of polyphenylene oxides.

As the result of detailed studies, the inventors have further found the following fact: that is, in a process for polymerizing a styrene type compound in a solvent in the presence of a radical-initiator as a catalyst, the conversion is greatly affected by the monomer concentration, and a conversion of more than 80% cannot be attained unless the monomer concentration is more than 70% by weight, and if the monomer concentration is less than 70% by weight, e.g. 20% by weight, the conversion does not reach more than about 25%. Accordingly, the above-mentioned process is commercially disadvantageous. Further, in polymerizing a styrene compound in the presence of a polyphenylene oxide, the polyphenylene oxide inhibits or suppresses the polymerization of the styrene compound since said polyphenylene oxide contains a phenolic hydroxyl group, and the conversion of the styrene type compound is made lower than in the case where the polymerization is effected in the absence of polyphenylene oxide. Particularly when the amount of the polyphenylene oxide is large, there are some cases where the polymerization does not progress at all.

Such phenomena as mentioned above are ob-

served also in the case where styrene is polymerized in an aqueous dispersion system in the presence of a polyphenylene oxide, and it has been found that the polymerization progresses only in the case where the amount of polyphenylene oxide is considerably smaller than that of styrene. The same phenomena as above are observed also in the case where styrene is polymerized in an aqueous dispersion system in the presence of a polyphenylene oxide and a rubber component.

The inventors experimentally carried out the polymerization of a styrene type compound in a dispersed state in an aqueous medium containing a surface active agent and a catalyst in the presence of a polyphenylene oxide and a rubbery polymer, but the dispersed state was so poor as to make impossible the smooth progress of polymerization. This experiment is set forth below as Referential Example.

Referential Example

Into a 200 ml flask equipped with a thermometer, a nitrogen-injecting pipe and a condenser was charged a mixture of poly-2,6-dimethyl - 1,4 - phenylene oxide (hereinafter referred to as "the polyether"), a polybutadiene rubber obtained by salting out JSR 0700 produced by Japan Synthetic Rubber Co. and styrene. Into the flask, nitrogen gas was injected, while stirring the mixture, to exclude oxygen present in the system. Subsequently, 1.0% by weight based on the styrene of benzoyl peroxide was added as a catalyst, and then nitrogen gas was sufficiently injected into the flask to exclude the oxygen. Thereafter, an aqueous solution containing sodium stearate as a surface active agent was added, and the resulting dispersion system was reacted with vigorous stirring at 80°C for 10 hours.

After completion of the reaction, hydrochloric acid was added to separate the reaction liquid, and the organic layer was charged into methanol to precipitate a polymer, which was then filtered, washed and dried. The thus obtained polymer was extracted under reflux with acetone containing 15—20 wt % of cyclohexane, was filtered and was then extracted with fresh acetone containing 15—20 wt % of cyclohexane. This operation was repeated 10 times and the extraction was effected for 30 hours to obtain a graft polymer as an extraction residue. From the amount of the thus obtained graft polymer, styrene graft conversion and styrene graft efficiency were calculated according to the following equations:

$$\text{Styrene graft conversion } (\%) = \frac{\begin{pmatrix}\text{Weight}\\ \text{of graft}\\ \text{polymer}\end{pmatrix} - \begin{pmatrix}\text{Weight} & & \text{Weight of}\\ \text{of fed} & + & \text{fed poly-}\\ \text{polyether} & & \text{butadiene}\end{pmatrix}}{\text{Weight of fed styrene}} \times 100$$

$$\text{Stryene graft efficiency } (\%) = \frac{\begin{pmatrix}\text{Weight}\\ \text{of graft}\\ \text{polymer}\end{pmatrix} - \begin{pmatrix}\text{Weight} & & \text{Weight of}\\ \text{of fed} & + & \text{fed poly-}\\ \text{polyether} & & \text{butadiene}\end{pmatrix}}{\begin{pmatrix}\text{Weight}\\ \text{of total}\\ \text{polymer}\end{pmatrix} - \begin{pmatrix}\text{Weight} & & \text{Weight of}\\ \text{of fed} & + & \text{fed poly-}\\ \text{polyether} & & \text{butadiene}\end{pmatrix}} \times 100$$

The results obtained were as shown in Table 1.

TABLE 1

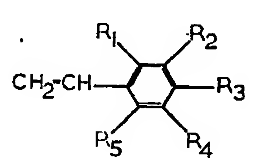
Run No.	Styrene (g)	Polyether (g)	Rubber (g)	Water (g)	Surface active agent (g)	Styrene graft conversion (%)	Styrene graft efficiency (%)
1	10	10	1	20	0	slight	0
2	10	10	1	20	2	slight	0
3	10	15	1	30	0	slight	0
4	10	15	1	30	2	slight	0

Thus, in polymerizing according to the known process a styrene compound dispersed in an aqueous medium in the presence of a polyphenylene oxide and a rubber component, the styrene compound should be used at a high concentration and in an amount greater than that of the polyphenylene oxide, as disclosed in Dutch Patent Application No. 66—17529. (According to the process of said Dutch patent application, styrene is used in at least 8 times the amount of polyether.) Accordingly, when the conversion is made high, the resulting polymerization product comes to contain a large amount of the styrene compound and thus is deprived of the excellent properties of the polyphenylene oxide. If the excellent properties of the polyphenylene oxide are desired to be maintained, the conversion of the styrene compound should be made low. Thus, the conventional process is economically disadvantageous.

It is well known that if the components are the same, a mixture and a graft polymer high in graft efficiency are greatly different from each other in properties, in general. Accordingly, there has been desired the advent of a graft polymer comprising a styrene type compound, a polyphenylene oxide and a rubber component which is higher in graft efficiency of the styrene type compound.

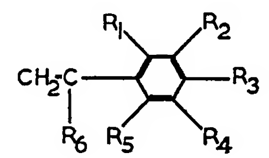
As the result of various studies on processes for polymerizing styrene in the presence of a polyphenylene oxide and a rubber component, the present inventors found that a graft polymer high in polyphenylene oxide content and high in graft efficiency of styrene type compound can be produced by polymerizing the aforesaid components in a dispersed state in an aqueous medium containing a solvent for the polyphenylene oxide, a surface active agent and a free radical initiator. The present invention has been attained on the basis of the above-mentioned finding.

According to the present invention, a process for the production of graft polymers comprises polymerizing a dispersion of a styrene component comprising a compound of the formula,



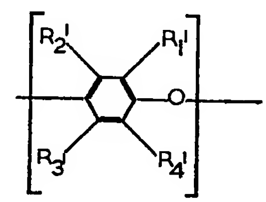
(IIa)

in which R_1, R_2, R_3, R_4 and R_5 are the same or are different and each is a hydrogen atom, halogen atom or a cyano, nitro, amino, substituted amino, hydroxyl, carboxyl, hydrocarbon, substituted hydrocarbon, hydrocarbonoxy or substituted hydrocarbonoxy group, alone or in combination with a compound of the formula,



(IIb)

wherein R_1, R_2, R_3, R_4 and R_5 have the meaning defined above; and R_6 is a hydrocarbon group, the styrene component being present in an amount of from 0.3 to 10 parts by weight per part by weight of a polyphenylene oxide as defined below, in the presence of from 0.01 to 1 part by weight of a rubbery polymer per part by weight of a rubbery polymer per part by weight of a polyphenylene oxide as defined below, and a polyphenylene oxide having a repeating unit of the formula,



(I)

wherein R_1', R_2', R_3' and R_4' are the same or are different and each is a hydrogen or a halogen atom, or a hydrocarbon, substituted hydrocarbon, cyano, hydrocarbonoxy, substituted hydrocarbonoxy, or nitro group, in an aqueous medium containing a solvent for the poly-phenylene oxide, an anionic or non ionic surface active agent and a free radical initiator, the solvent being present in an amount of from 0.5 to 20 parts by weight per part by weight of the polyphenylene oxide.

Examples of the polphenylene oxides include poly - 2,6 - dimethyl - 1,4 - phenylene oxide, poly - 2,6 - diethyl - 1,4 - phenylene oxide, poly - 2,6 - dipropyl - 1,4 - phenylene oxide, poly - 2 - methyl - 6 - allyl - 1,4 - phenylene oxide, poly - 2,6 -dimethoxy - 1,4 - phenylene oxide, poly - 2,6 - dichloromethyl - 1,4 - phenylene oxide, poly - 2,6 - dibromomethyl - 1,4 - phenylene oxide, poly - 2,6 - ditolyl - 1,4 - phenylene oxide, poly - 2,6 - dichloro - 1,4 - phenylene oxide, poly - 2,5 - dimethyl - 1,4 - phenylene oxide and poly - 2,6 - diphenyl - 1,4 - phenylene oxide.

Examples of rubbery polymers usable in the present invention include polybutadiene, polyisoprene (including natural rubber), polychloroprene, butadiene-styrene copolymer, butadiene-styrene block copolymer, poly-butadiene-styrene graft copolymer, polyisoprene-styrene graft copolymer, isoprene-styrene copolymer, poly (butadiene-acrylonitrile)-styrene graft co-

polymer, butadiene-acrylonitrile copolymer, poly(butadiene-styrene) - α - methylstyrene graft copolymer, poly(butadiene-styrene)-methacrylate graft copolymer, poly(butadiene-styrene)-styrene graft copolymer, poly(butadiene-styrene) - styrene - acrylonitrile graft copolymer, polychloroprene-styrene graft copolymer and poly(butadiene-acrylonitrile) - styrene graft copolymer.

R_1, R_2, R_3, R_4 and R_5 may be hydrogen, chlorine, bromine and iodine atoms, hydroxy, carboxyl, methyl, ethyl, propyl, allyl, phenyl, benzyl, methylbenzyl, chloromethyl, bromomethyl, cyanoethyl, cyano, nitro, amino, methoxy, ethoxy, chloromethoxy, phenoxy, and p-chlorophenoxy groups; and R_6 may be a methyl group.

Examples of the styrene type compounds include styrene, 2,4 - dichlorostyrene, p - carboxyl styrene, p - nitrostyrene, p - methoxystyrene, o - methylstyrene, p - methylstyrene, p - phenylstyrene, p - acetoxystyrene, p - aminostyrene, m - cyanostyrene, p - chlorostyrene, o - hydroxystyrene, p - hydroxystyrene, o - divinylbenzene, p - divinylbenzene, α - methylstyrene, p - methoxy - α - methylstyrene, p - methyl - α - methylstyrene, m - methyl - α - methylstyrene, o - methyl - α - methylstyrene, and 1,1 - diphenylethylene.

The styrene type compounds represented by the formula (IIb) are preferably used in an amount of less than 40% by weight based on the total styrene amount.

The aqueous medium contain a dispersion stabilizer.

Examples of such free radical initiators include octanoyl peroxide, decanoyl peroxide, stearoyl peroxide, lauroyl peroxide, 2,5 - dimethyl - 2,5 - di(tert - butyl)hexane, 3,5,5 - trimethyl - hexanoyl peroxide, 2,4 - dichlorobenzoyl peroxide, benzoyl peroxide, tert-butyl peroxybenzoate, tert-butylperoxyisobutyrate, tert-butyl peroxyacetate, tert - butyl peroxy - pivalate, diisopropylbenzene hydroperoxide, di-tert-butyl peroxide, 2,5 - bis(tert-butyl-peroxy) butane, cyclohexanone peroxide, methyl ethyl ketone peroxide, dicumyl peroxide, α,α' - azobisisobutyronitrile, hydrogen peroxide, potassium persulphate, ammonium persulphate and sodium perborate. These radical-initiators may be used in combinations of 2 or more. In order to attain sufficiently high polymerization rates at low temperatures, it is sometimes advantageous to use redox type catalysts prepared by adding reducing agents to the above-mentioned radical-initiator. Frequently employed reducing agents include glucose, fructose, ammonium ferrous sulphate, sodium hydrogensulphate, N,N - dimethylaniline, tetraethylenepentamine, p - chlorobenzenesulphinic acid, benzoin, acetoin, glyceraldehyde and dioxyacetone. These catalysts may be used in combinations of 2 or more, and may be incorporated with such additives as sodium pyrophosphate, sodium hydrogenphosphate, etc. The catalysts are preferably used in an amount of 0.01—5% by weight based on the amount of styrene type compound.

The surface active agent employed in the present invention may be suitably selected from anionic and nonionic surface active agents. Particularly preferable surface active agents usable in the present invention are alkali metal salts of higher fatty acids, alkali metal salts of alkylbenzenesulphonic acids, fatty acid esters of polyoxyethylene and alkyl ethers of polyoxyethylene. Concrete examples of particularly effective surface active agents include sodium stearate, potassium stearate, sodium oleate, sodium palmitate, sodium myristate, sodium laurate, potassium laurate, sorbitan monolaurate, sodium dodecylbenzenesulphonate, polyoxyethylene monooleate, polyoxyethylene distearate, polyoxyethylene monolaurate, polyoxyethylene lauryl ether and polyoxyethylene - 9 - octadecene ether. These surface active agents may be used in combinations of 2 or more. The surface active agents are not particularly limited in amount employed, but are preferably used in a proportion of 0.01-5% by weight based on the amount of water.

These surface active agents may be used in combination with dispersion stabilizers such as, for example, polyvinyl alcohol, methyl cellulose, carboxymethyl cellulose, hydroxymethyl cellulose, starch, agar, sodium glycolate, calcium carbonate, calcium phosphate, magnesium carbonate, talc and bentonite.

Solvents usable in the present invention may be any of those which dissolve the polyphenylene oxides but are insoluble in water, and are inert to the polymerization reaction. These solvents are not particularly required to be good solvents for the rubbery polymers employed. Examples of such solvents include benzene, toluene, xylene and the like aromatic hydrocarbons; chlorobenzene, nitrobenzene and the like halogen- or nitro-substituted compounds of aromatic hydrocarbons; and chloroform, carbol tetrachloride and the like halogenated hydrocarbons. These solvents are used in an amount of 0.5—20 times, preferably 1—10 times, the weight of the polyphenylene oxides.

Water may be used in optional amount, but is ordinarily used in an amount of 0.5—10 times, preferably 1—6 times, the total weight of the polyphenylene oxide, the rubbery polymer, the styrene type compound and the solvent.

In the present invention, the order and manner of addition of polyphenylene oxide, rubbery polymer, styrene type compound, surface active agent, catalyst and other reaction reagents are not restricted. For example, there may be adopted such procedures that the styrene type compound is added to a solution containing the polyphenylene oxide and the rubbery polymer, and then the resulting mixture is charged with an aqueous solution containing the catalyst and the surface active

agent; or that water is charged with the styrene compound and a solution containing the polyphenylene oxide and the rubbery polymer, and then the catalyst and the surface active agent are added to the resulting mixture.

In the present method, the rubbery polymer may be used not only in the form of rubber itself but also in the form of a solution of a latex. The rubbery polymer may be added at the initial stage of the reaction, as mentioned above, or may be added at a suitable stage during the polymerization reaction in order to vary the extent of contribution of the rubbery polymer to the graft polymerization, taking the properties of the resulting modified polyphenylene oxide into consideration. This is decided according to the interrelation with the gelation ratio, molecular weight and other physical properties or the amount of the rubbery polymer added.

In producing, for example, an impact resistant modified polyphenylene oxide according to the present method, it is desirable that the rubbery polymer takes part in the graft-polymerization, while maintaining a suitable particle diameter. The preferable particle diameter of the rubbery polymer is from 0.1μ to 10μ.

In the present invention, the polymerization reaction temperature is not particularly limited in so far as the reaction mixture is in the form of a liquid, but is preferably from 40° to 150°C. Further, the reaction can be effected not only at normal pressure but also under pressure or under reduced pressure.

If, in the present invention, oxygen is present in the reaction system, the polymerization rate, the graft efficiency and the like are adversely affected. Generally, therefore, it is desirable to carry out the reaction in an inert gas atmosphere or under reduced pressure. This, however, does not mean that the oxygen should be completely removed during the polymerization reaction, because the polymerisation proceeds at a significant rate even in the presence of a small amount of oxygen.

According to the present invention, the molecular weight of the styrene type compound grafted on the polyphenylene oxide and the rubbery polymer can be controlled by varying the concentrations of the styrene type compound, the polyphenylene oxide, the rubbery polymer and the catalyst. Alternatively, however, said molecular weight may be controlled by addition of a chain transfer agent employed in an ordinary polymerization reaction. Such chain transfer agents include mercaptans and alcohols. By controlling the molecular weight of the grafted styrene type compound and the number of grafted branches, the physical properties of the grafted polyphenylene oxide can be varied.

After completion of the reaction, the polymer may be recovered in such a manner that the reaction mixture as it is, or only an oil layer separated by salting out the reaction mixture, is charged into a poor solvent for the polymer, or such poor solvent is added to the reaction mixture or to said oil layer, to deposit the polymer, followed by drying. Alternatively, the polymer may be recovered by directly subjecting the reaction mixture or said oil layer to hot air-drying or spray-drying.

Graft polymers produced in accordance with the present invention have been improved in flow property and enhanced, at the same time, in oxidation and impact resistance, without any substantial change in properties inherent to polyphenylene oxides. That is, in accordance with the present invention, there are obtained, without any treatment of free hydroxyl groups of polyphenylene oxides, graft polymers which do not substantially change in color tone at the time of heating, are high in resistance to oxidation at elevated temperatures, and are higher in impact resistance and elongation than polyphenylene oxides.

The present invention is illustrated below with reference to examples. In the examples, percentages are by weight unless otherwise indicated.

Example 1

In a 500 ml flask equipped with a thermometer, a nitrogen-injecting pipe and a condenser, 16 g of poly - 2,6 - dimethyl - 1,4 - phenylene oxide ($[\eta]$ = 0.65 dl/g in chloroform at 25°C), which had been obtained by oxidation coupling reaction using manganese chloride (II)-sodium methylate as a catalyst, was dissolved in 48 g of industrial xylene, and then 1.6 g of a polybutadiene prepared by salting out JSR 0700 (trade name of a rubber produced by Japan Synthetic Rubber Co.) was dissolved in the resulting solution. To this solution were added 16 g of styrene, 192 g of distilled water, 3.4 g of sodium stearate as a surface active agent, and a mixture of 0.2 g of benzoyl peroxide and 0.074 g of glucose as a catalyst. Subsequently, nitrogen gas was injected into the flask, while dispersing the mixture with vigorous stirring (620 r.p.m.), to exclude oxygen present in the system, and then the mixture was reacted with stirring at 80°C for 5 hours. After completion of the reaction, the reaction product was salted out by addition of 4 ml of concentrated hydrochloric acid. Thereafter, the organic layer was charged into 500 ml of methanol, and the resulting precipitate was recovered by filtration to obtain 31.2 g of a white polymer.

The thus obtained polymer was extracted for 30 hours with hot acetone containing 15—20% by weight of cyclohexane, whereby 29.2 g of acetone containing 15—20% by weight of cyclohexane insoluble portion was obtained. From this were calculated the values of such physical properties as styrene graft conversion, styrene graft efficiency, proportion of bonded styrene based on the total polymer, etc. These values are shown in Table 3.

In Table 2, there is shown a comparison of the physical property values of the above-mentioned graft polymer with those of a mixture prepared by solution-blending 55.2 parts by weight of the polyphenylene oxide ([η] = 0.65 dl/g in chloroform at 25°C) and 5.0 parts by weight of the polybutadiene both employed in the above-mentioned reaction, and 39.8 parts by weight of polystyrene ($\bar{M}w$ = 270,000).

TABLE 2

	Graft polymer	Mixture
Charpy impact value (Kg.cm/cm^2)	12.3	4.1
Vicat softening point (°C)	140	121
Modulus of tensile elasticity (Kg/cm^2)	10,000	8,300

The test pieces were prepared by rolling at 220—230°C for 5 minutes and then hot-pressing at 220°C under pressure of 100 Kg/cm^2 for 10 minutes.

Impact test was carried out according to JIS—6745 (notched, 20°C).

Vicat softening point was measured according to ASTM—D—1525—65T.

Tensile test was carried out according to JIS—6745 at a tensile speed of 10 mm/min. (20°C.)

Example 2

Example 1 was repeated, except that 2.6 g of a polybutadiene latex (JSR 0700 produced by Japan Synthetic Rubber Co., solid content 60%) was used as the polybutadiene, to obtain 31.0 g of a white polymer.

The thus obtained polymer was treated in the same manner as in Example 1. The characteristic values of the polymerization and the physical property values of the polymer are shown in Table 3.

Example 3

Example 1 was repeated, except that in place of the 1.6 g polybutadiene, 2.6 g of a polybutadiene latex (JSR 0700 produced by Japan Synthetic Rubber Co.; solid content 60%) was added to the reaction system 4½ hours after initiation of the polymerisation, to obtain 31.7 g of a white polymer.

The thus obtained polymer was treated in the same manner as in Example 1. The characteristic values of the polymerization and the physical properties of the polymer are shown in Table 3.

Example 4

Examples 1, 2 and 3 were repeated, except that a mixture of 0.2 g of potassium persulphate and 0.3 g of sodium hydrogensulphite was used as the catalyst, to obtain 31.2 g, 29.3 g and 31.2 g of white polymers, respectively.

The thus obtained polymers were treated in the same manner as in Example 1. The characteristic values of the polymerization and the physical properties of the individual polymers are shown in Table 3, columns 4—1, 4—2 and 4—3, respectively.

Example 5

Examples 1, 2 and 3 were repeated, except that a mixture of 0.164 g of 3,5,5 - trimethylhexanoyl peroxide and 0.088 g of tert-butyl peroxybenzoate was used in place of the benzoyl peroxide, to obtain white polymers.

The thus obtained polymers were treated in the same manner as in Example 1. The results are shown in Table 3, columns 5—1, 5—2 and 5—3, respectively.

Example 6

Example 1 was repeated, except that 3.0 g of a polybutadiene-styrene graft copolymer latex (solid content 60%, bonded styrene content 25%) was used as the rubbery polymer and a mixture of 10 g of styrene and 6 g of α - methyl - p - methylstyrene was used in place of 16 g of styrene, to obtain a white polymer. The results are shown in Table 3.

Example 7

Example 1 was repeated, except that 1.9 g of a polybutadiene-styrene graft copolymer (bonded styrene content 25%) was used in place of the polybutadiene. The results are shown in Table 3.

Example 8

Examples 2 and 3 were repeated, except that 3.0 g of a polybutadiene-styrene graft copolymer latex (solid content 60%, bonded styrene content 25%) was used in place of the polybutadiene latex. The results are shown in Table 3, columns 8—1 and 8—2, respectively.

Example 9

Example 2 was repeated, except that a mixture of 8 g of styrene and 8 g of p-methoxystyrene was used in place of 16g of styrene. The results are shown in Table 3.

Example 10

Example 2 was repeated, except that poly-2,6 diethyl - 1,4 - phenylene oxide having a molecular weight of 70,000 was used in place of the poly - 2,6 - dimethyl - 1,4 - phenylene oxide. The results are shown in Table 3.

TABLE

Example	1	2	3	4—1	4—2	4—3
Styrene graft conversion (wt. %)	72.5	68.8	70.0	55.3	53.6	50.1
Styrene graft efficiency (wt. %)	85.3	81.5	79.0	65.0	67.0	59.0
Proportion of bonded styrene based on total polymer (wt %)	39.8	38.1	38.8	33.6	32.9	32.0
Proportion of butadiene based on total polymer (wt %)	5.0	5.5	5.4	5.9	6.0	6.1
Charpy impact value (kg./cm/cm^2)	12.3	11.9	12.3	11.7	12.5	13.0
Vicat softening point (°C.)	140	139	141	145	145	147
Modulus of tensile elasticity (kg/cm^2)	10,000	9,900	9,200	10,000	10,000	10,000

3

5—1	5—2	5—3	6	7	8—1	8—2	9	10
72.3	68.0	74.0	70.0	70.2	69.0	72.5	75	72
85.0	83.0	87.0	75.0	82.0	84.0	86.0	88	85
39.7	40.1	40.3	41.2	40.3	40.0	41.3	40.7	42.1
5.3	5.5	5.3	5.0	5.0	4.7	4.6	5.3	5.7
13.8	12.0	12.8	13.0	13.3	14.1	14.0	13.0	12.7
143	140	140	148	142	142	139	142	138
9,700	9,900	9,800	9,500	10,000	11,000	10,000	9,750	10,000

Example 11

Example 2 was repeated, except that each of the compounds set forth in Table 4 was used as the surface active agent. The results are shown in Table 4.

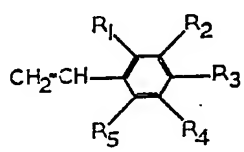
TABLE 4

Run No.	Surface active agent	Monomer conversion (%)	Graft conversion (%)	Graft efficiency (%)
1	Sodium stearate	84.5	68.8	81.5
2	Sodium myristate	80.0	70.0	89.9
3	Sorbitan monolaurate	12.5	6.0	48.0
4	Lauryl trimethylammonium chloride	0	0	0
5	Polyoxyethylene alkylamine	0	0	0
6	Sodium carboxymethyl cellulose	0	0	0
7	10:1 Sodium stearate-sodium carboxymethyl cellulose mixture	83.8	69.5	83.0

Runs 4, 5 and 6 are included for the purpose of comparison to show that cationic surface active agents are ineffective.

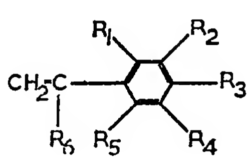
WHAT WE CLAIM IS:—

1. A process for the production of graft polymers which comprises polymerizing a dispersion of a styrene component comprising a compound of the formula,



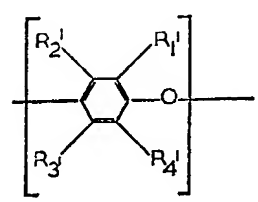
(IIa)

in which R_1, R_2, R_3, R_4 and R_5 are the same or are different and each is a hydrogen atom, a halogen atom or a cyano, nitro, amino, substituted amino, hydroxyl, carboxyl, hydrocarbon, substituted hydrocarbon, hydrocarbonoxy or substituted hydrocarbonoxy group, alone or in combination with a compound of the formula,



(IIb)

wherein R_1, R_2 R_3, R_4 and R_5 have the meaning defined above; and R_6 is a hydrocarbon group, the styrene component being present in an amount of from 0.3 to 10 parts by weight per part by weight of a polyphenylene oxide as defined below, in the presence of from 0.01 to 1 part by weight of a rubbery polymer per part by weight of a polyphenylene oxide as defined below, and a polyphenylene oxide having a repeating unit of the formula,



(I)

wherein R_1', R_2', R_3' and R_4' are the same or are different and each is a hydrogen or a halogen atom, or a hydrocarbon, substituted hydrocarbon, cyano, hydrocarbonoxy, substituted hydrocarbonoxy, or nitro group, in an aqueous medium containing a solvent for the polyphenylene oxide, an anionic or non-ionic surface active agent and a free radical initiator, the solvent being present in an amount of from 0.5 to 20 parts by weight per part by weight of the polyphenylene oxide.

2. A process as claimed in Claim 1, wherein the compound of formula II(a) is styrene, *p*-

methylstyrene, *o*-methylstyrene, *p*-methoxystyrene, *p*-aminostyrene, *p*-chlorostyrene or *o*-hydroxy styrene.

3. A process as claimed in Claim 1 or Claim 2 wherein the compound of formula II(b) is α - methylstyrene, p - methyl - α - methylstyrene, m - methyl - α - methylstyrene or *o* - methyl - α - methylstyrene.

4. A process as claimed in any one of the preceding claims wherein the compound of formula II(b) is used in an amount less than 40% by weight of the styrene component.

5. A process as claimed in any one of the preceding claims wherein the rubbery polymer is polybutadiene, polyisoprene, polychloroprene, a polybutadiene-styrene graft copolymer, a butadiene - styrene copolymer, a butadiene-styrene block copolymer or a poly(butadiene - styrene) - styrene graft copolymer.

6. A process as claimed in any one of the preceding claims wherein the polyphenylene oxide is poly(2,6-dimethyl-1,4-phenylene oxide).

7. A process as claimed in any one of the preceding claims wherein the surface active agent is sodium stearate, potassium stearate, sodium myristate, sodium laurate, potassium laurate, sorbitan mono-laurate, polyoxymethylene monolaurate, polyoxyethylene lauryl ether, sodium dodecylbenzene-sulphonate or polyoxyethylene - 9 - octadecene ether.

8. A process as claimed in any one of the preceding claims wherein the initiator is benzoyl peroxide, 3,5,5-trimethylhexanoyl peroxide, lauroyl peroxide, dicumyl peroxide, tert-butyl peroxybenzoate or potassium persulphate.

9. A process as claimed in Claim 8, wherein the radical-initiator is used together with a reducing agent which is sodium hydrogensulphate, benzoin, dioxyacetone or glyceraldehyde.

10. A process as claimed in any one of the preceding claims wherein the solvent is benzene, toluene or xylene.

11. A process as claimed in Claim 1 substantially as hereinbefore described with reference to any of the Examples.

12. Modified polyphenylene oxides when obtained by a process as claimed in any one of Claims 1—11.

MARKS & CLERK.

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